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## A local-density formulation for NMR parameters in metals

J J van der Klink

Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, PHB-Ecublens, CH-1015 Lausanne, Switzerland

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**Abstract.** The local-density approximation to the expression for the generalized complex spin susceptibility is used to treat simultaneously the effects of core polarization and of susceptibility enhancement on the Knight shift and on the nuclear spin–lattice relaxation rate in metals. The resulting equations can be considered as refinements of the Yafet–Jaccarino (YJ) theory for transition metals, and retain the structure of a sum of terms related to partial densities of states at the Fermi level. The original YJ theory correctly identified the importance of core polarization, but was unable to provide good fits to experimental data in transition metals (specifically Pt and Pd). To obtain satisfactory agreement, later workers found it necessary to introduce empirically factors taking account of enhancement effects. This paper provides a theoretical basis for doing so.

The effect of the Fermi contact interaction between nuclear and electronic spins on the NMR parameters of the nuclei (Knight shift, relaxation rate and Ruderman–Kittel coupling) in paramagnetic systems can be described in quite a general way (valid in metals, semiconductors or molecules) through the complex generalized electron spin susceptibility  $\chi(\mathbf{r}, \mathbf{r}'; \omega) = \chi'(\mathbf{r}, \mathbf{r}'; \omega) - i\chi''(\mathbf{r}, \mathbf{r}'; \omega)$ , that describes the local response of the spin magnetization in  $\mathbf{r}$  to a time-varying magnetic field  $H(\mathbf{r}') \cos(\omega t)$  applied in  $\mathbf{r}'$ . In NMR we are usually concerned with the  $\omega \rightarrow 0$  limit of  $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ , and the  $\omega$ -argument will not be written in the following. The uniform susceptibility of the sample  $\bar{\chi}'$ , the Knight shift  $K$  of a nucleus at site  $\mathbf{R}$  and its spin–lattice relaxation rate  $T_1^{-1}$  at temperature  $T$  are given by

$$\bar{\chi}' = V^{-1} \iint \chi'(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (1)$$

$$K = (2/3) \int \chi'(\mathbf{R}, \mathbf{r}') d\mathbf{r}' \quad (2)$$

$$S(T_1 T)^{-1} = 2\mu_0(2\mu_B/3)^2 \chi''(\mathbf{R}, \mathbf{R})(\pi\hbar\omega)^{-1} \quad (3)$$

where  $S$  is the Korringa constant  $(\gamma_e/\gamma_n)^2(\hbar/4\pi k_B)$  and  $\mu_B$  the Bohr magneton. To obtain CGS expressions, replace the factors  $2/3$  in the right-hand sides of (2) and (3) by  $8\pi/3$ .

In the following we will be concerned with metals [1, 2], where the effects are at most only slightly temperature dependent, and  $\chi$  will be evaluated at zero temperature. In a spirit similar to that of the paper by Yafet and Jaccarino [3], the aim is not to obtain absolute values for the Knight shift and the relaxation rate, but only to show how the Korringa relation between  $(T_1 T)^{-1}$  and  $K^2$  is modified by band structure and exchange enhancement. We assume that as results of a band structure calculation, the one-electron energies  $\varepsilon_i$  and wavefunctions  $\psi_i(\mathbf{r})$  are known. The Fermi energy is taken as zero, and

the position vectors are written as  $\mathbf{r} = \boldsymbol{\rho} + \mathbf{R}_\alpha$  with  $\boldsymbol{\rho}$  restricted to the Wigner–Seitz (WS) cell at the origin, and  $\mathbf{R}_\alpha$  ( $\alpha = 1, \dots, N$ ) a lattice vector. The  $\psi_i(\mathbf{r})$  are supposed to be given by muffin-tin orbitals  $\Phi_i(\boldsymbol{\rho})$ ; the WS cell is approximated by a sphere and the  $\Phi_i$  are developed in spherical harmonics  $Y_{lm}$ :

$$\psi_i(\mathbf{r}) = N^{-1/2} \Phi_i(\boldsymbol{\rho}) \exp(i\mathbf{k}_i \cdot \mathbf{R}_\alpha) \quad (4a)$$

$$\Phi_i(\boldsymbol{\rho}) = (4\pi)^{1/2} \sum_{lm} C_{lm}(i) \phi_l(\varepsilon_i, \rho) Y_{lm}(\theta, \phi) \quad (4b)$$

where the function  $\phi_l$  is real, and depends on the index  $i$  only through the energy  $\varepsilon_i$ . The  $\psi_i(\mathbf{r})$  are normalized in the volume  $V$  of the sample; the  $\Phi_i(\boldsymbol{\rho})$  in the WS cell of volume  $\Omega = V/N$ . The  $lm$ -like partial densities of electron states (twice the number of electron energy levels per atom and per unit energy interval) at energy  $\varepsilon$ ,  $D_{lm}(\varepsilon)$ , obey Obata's sum rule [4]:

$$2N^{-1} \sum_i \delta(\varepsilon - \varepsilon_i) C_{lm}^*(i) C_{l'm'}(i) = D_{lm}(\varepsilon) \delta_{ll'} \delta_{mm'}. \quad (5)$$

In the following, the energy argument in  $D(\varepsilon)$  and in  $\phi_l(\varepsilon, \rho)$  will be omitted when  $\varepsilon = 0$  (the Fermi energy).

The expressions for the unenhanced (or Pauli) value of the susceptibilities (index  $P$ ) are

$$(2\mu_0\mu_B^2)^{-1} \chi'_p(\boldsymbol{\rho}, \boldsymbol{\rho}' + \mathbf{R}_\alpha) = N^{-2} \sum_i \delta(\varepsilon_i) |\Phi_i(\boldsymbol{\rho})|^2 |\Phi_i(\boldsymbol{\rho}')|^2 \\ + N^{-2} \sum_{ij} I(\varepsilon_i, \varepsilon_j) \Phi_i(\boldsymbol{\rho}) \Phi_i^*(\boldsymbol{\rho}') \Phi_j^*(\boldsymbol{\rho}) \Phi_j(\boldsymbol{\rho}') \exp[i(\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{R}_\alpha] \quad (6a)$$

$$(2\mu_0\mu_B^2\pi\hbar\omega)^{-1} \chi''_p(\boldsymbol{\rho}, \boldsymbol{\rho}' + \mathbf{R}_\alpha) = N^{-2} \sum_{ij} \delta(\varepsilon_i) \delta(\varepsilon_j) \Phi_i(\boldsymbol{\rho}) \Phi_i^*(\boldsymbol{\rho}') \Phi_j^*(\boldsymbol{\rho}) \Phi_j(\boldsymbol{\rho}') \\ \times \exp[i(\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{R}_\alpha] \quad (6b)$$

where  $I(\varepsilon_i, \varepsilon_j) = 0$  if  $\varepsilon_i = \varepsilon_j$ , and  $(\theta(\varepsilon_i) - \theta(\varepsilon_j))/(\varepsilon_i - \varepsilon_j)$  otherwise.

Due to electron–electron interactions, the actual value  $\chi(\mathbf{r}, \mathbf{r}')$  of the susceptibility is different from the unenhanced value  $\chi_p(\mathbf{r}, \mathbf{r}')$ . In the local-density approximation of the density-functional theory of the inhomogeneous electron gas, the paramagnetic susceptibility is given by the solution of the integral equation [5–8]

$$\chi(\mathbf{r}, \mathbf{r}') = \chi_p(\mathbf{r}, \mathbf{r}') + \int \chi_p(\mathbf{r}, \mathbf{r}_1) v(n(\mathbf{r}_1)) \chi(\mathbf{r}_1, \mathbf{r}') d\mathbf{r}_1 \quad (7)$$

where  $v$  is a function only of the charge density  $n(\mathbf{r}_1)$  at position  $\mathbf{r}_1$ , and will be written as  $v(\mathbf{r}_1)$  in the following. The theory is in principle restricted to ground-state properties, but it is believed that its results for low-lying excitations are reasonably correct [8]: to lowest order in  $\hbar\omega$ , (7) will be used for the complex susceptibility  $\chi = \chi' - i\chi''$ . The real part  $\chi'$  is

$$\chi'(\boldsymbol{\rho}, \boldsymbol{\rho}' + \mathbf{R}_\alpha) = \chi'_p(\boldsymbol{\rho}, \boldsymbol{\rho}' + \mathbf{R}_\alpha) \\ + \sum_\beta \int \chi'_p(\boldsymbol{\rho}, \boldsymbol{\rho}_1 + \mathbf{R}_\beta) v(\boldsymbol{\rho}_1) \chi'(\boldsymbol{\rho}_1, \boldsymbol{\rho}' + \mathbf{R}_\alpha - \mathbf{R}_\beta) d\boldsymbol{\rho}_1. \quad (8a)$$

Once  $\chi'$  has been found,  $\chi''$  can be calculated from

$$\chi''(\boldsymbol{\rho}, \boldsymbol{\rho}' + \mathbf{R}_\alpha) = \chi''_p(\boldsymbol{\rho}, \boldsymbol{\rho}' + \mathbf{R}_\alpha) \\ + 2 \sum_\beta \int \chi''_p(\boldsymbol{\rho}, \boldsymbol{\rho}_1 + \mathbf{R}_\beta) v(\boldsymbol{\rho}_1) \chi'(\boldsymbol{\rho}_1, \boldsymbol{\rho}' + \mathbf{R}_\alpha - \mathbf{R}_\beta) d\boldsymbol{\rho}_1$$

$$\begin{aligned}
& + \sum_{\beta} \sum_{\gamma} \int \int \chi'(\boldsymbol{\rho}, \boldsymbol{\rho}_1 + \mathbf{R}_{\beta}) v(\boldsymbol{\rho}_1) \chi_p''(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2 + \mathbf{R}_{\gamma} - \mathbf{R}_{\beta}) \\
& \times v(\boldsymbol{\rho}_2) \chi'(\boldsymbol{\rho}_2, \boldsymbol{\rho}' + \mathbf{R}_{\alpha} - \mathbf{R}_{\gamma}) d\boldsymbol{\rho}_1 d\boldsymbol{\rho}_2. \quad (8b)
\end{aligned}$$

We assume that the magnetization  $m(\boldsymbol{\rho})$  induced by a uniform magnetic field has spherical symmetry:  $m(\boldsymbol{\rho}) = m(\rho)$ . Likewise we take the charge density  $n(\boldsymbol{\rho})$  as spherical, so that  $v(\boldsymbol{\rho}) = v(\rho)$ . To describe the relation between  $\chi$ ,  $K$  and  $T_1T$  it is useful to introduce a quantity  $m_l(\mathbf{q}; \boldsymbol{\rho})$  defined as

$$m_l(\mathbf{q}; \boldsymbol{\rho}) = \phi_l^2(\boldsymbol{\rho}) + \sum_{\alpha} \exp(-i\mathbf{q} \cdot \mathbf{R}_{\alpha}) \int \phi_l^2(\boldsymbol{\rho}_1) v(\boldsymbol{\rho}_1) \chi'(\boldsymbol{\rho}_1, \boldsymbol{\rho} + \mathbf{R}_{\alpha}) d\boldsymbol{\rho}_1. \quad (9)$$

It is probably a sufficient approximation to replace  $\chi'$  in (9) by  $\chi'_p$ , given by (6a).

The uniform susceptibility is calculated from (1) and (8a). Integration over the second argument on both sides of (8a), using the fact that  $\chi'(r_1, r_2) = \chi'(r_2, r_1)$ , gives

$$\int \chi'(\boldsymbol{\rho}, \mathbf{r}_1) d\mathbf{r}_1 \approx \mu_0 \mu_B^2 \sum_{lm} D_{lm} m_l(0; \boldsymbol{\rho}). \quad (10)$$

Now integrate  $m_l(0; \boldsymbol{\rho})$  according to (9) over  $\boldsymbol{\rho}$ , replacing  $\chi'$  in the right-hand side by (10). On both sides of the resulting equation, we suppose that  $m_l(0; \boldsymbol{\rho})$  in the integrals can be written as

$$m_l(0; \boldsymbol{\rho}) = (1 + A_l) \phi_l^2(\boldsymbol{\rho}). \quad (11a)$$

Performing the integration the  $A_l$  are found to be given by the system of equations

$$A_l = \sum_{l'm'} D_{l'm'} (1 + A_{l'}) v_{ll'} \quad (11b)$$

where

$$v_{ll'} = \mu_0 \mu_B^2 \int \phi_l^2(\rho) v(\rho) \phi_{l'}^2(\rho) d\rho. \quad (11c)$$

Supposing that the diagonal elements of  $v_{ll'}$  are much larger than the nondiagonal ones and using (1), (10) and (11a) finally leads to

$$\bar{\chi}' = \sum_{lm} \bar{\chi}'_{lm} = \mu_0 \mu_B^2 \Omega^{-1} \sum_{lm} D_{lm} \left[ 1 - v_{ll} \sum_{m'} D_{lm'} \right]^{-1}. \quad (12)$$

This is the dimensionless 'volume' susceptibility; to obtain the more frequently used CGS 'molar' susceptibility replace  $\mu_0$  by  $N_A \Omega$ .

The Knight shift becomes

$$K = \sum_{lm} K_{lm} = \sum_{lm} \bar{\chi}'_{lm} (\Omega H_{hf,l} / \mu_B) \quad (13)$$

where the 'l'-like effective hyperfine field  $H_{hf,l}$  is defined as

$$\Omega H_{hf,l} / \mu_B = 2m_l(0; 0) \left[ 3\Omega^{-1} \int m_l(0; \boldsymbol{\rho}) d\boldsymbol{\rho} \right]^{-1} \quad (14)$$

(in CGS, replace the factor 2/3 in (14) by  $8\pi/3$ ).

For the calculation of  $T_1T$  it is necessary to make an important approximation to (8b), similar to (but more general than) an approximation in the treatment by Yafet and Jaccarino [3] (see below). In the enhancement integrals on the right-hand side of (8b) only those contributions will be considered where both arguments of  $\chi_p''(\boldsymbol{\rho}, \boldsymbol{\rho}' + \mathbf{R})$  are in the same

WS cell. Furthermore,  $\chi_p''(\rho_1, \rho_2)$  is replaced by its spherical average, that depends only on  $|\rho_1| = \rho_1$  and  $|\rho_2| = \rho_2$ . Then we obtain from (8b) and (5)

$$2(\pi\hbar\omega\mu_0\mu_B^2)^{-1}\chi''(0,0) = \sum_{lm} D_{lm}^2 \left[ \phi_l^2(0)\phi_l^2(0) + 2\phi_l^2(0) \int \phi_l^2(|\rho_1|)v(|\rho_1|)\chi'(\rho_1,0) d\rho_1 \right. \\ \left. + \sum_{\alpha} \left[ \int \chi'(0, \rho_1 + \mathbf{R}_{\alpha})v(|\rho_1|)\phi_l^2(|\rho_1|) d\rho_1 \right]^2 \right]. \quad (15)$$

Using (15), (3) and (13) the relaxation rate can be written as

$$S(T_1T)^{-1} = \sum_{lm} k_l K_{lm}^2 \quad (16)$$

with the disenancement factors  $k_l$  defined by

$$k_l^{-1} = |m_l(0;0)|^2 / \left[ N^{-1} \sum_q |m_l(\mathbf{q};0)|^2 \right]. \quad (17)$$

The present results reduce to those in the Yafet and Jaccarino paper [3] by setting  $v_{ll} = 0$ ,  $k_l = 1$ . This is due a difference in approximations. They start by replacing  $\chi'$  in the right-hand sides of (8a) and (8b) with  $\chi_p'$  (6a). Next, they neglect 'the exchange integrals between two conduction band orbitals', which is equivalent to retaining only the  $I(\varepsilon_i, \varepsilon_j)$  sum on the right-hand side of (6a). As a consequence,  $v_{ll} = 0$ . Finally, 'only those configurations for which a core electron remains on the same atom are included', which is equivalent to considering only those contributions to the enhancement integrals where  $R_{\alpha} = 0$  in (6a). This results in  $k_l = 1$  and suppresses the  $q$ -dependence of  $m_l(\mathbf{q}; \rho)$  in (9).

The  $q$ -dependence of the susceptibility has been discussed for the homogeneous electron gas [9–12]. In that case, both  $m$  and  $v$  are position independent, and the hyperfine field is simply  $H_{hf} = 2\mu_B/3\Omega$ . The resulting expressions for (13) and (17) were given by Moriya [9]. It has been shown [10, 12] that experimental data for simple metals do not agree very well with the equations so obtained, but can be described satisfactorily using a theory of nonlocal interactions in the homogeneous electron gas. For that case, the relation between  $k$  and  $v$  is found to be roughly of the form

$$k \approx 1 - vD. \quad (18)$$

It would be interesting to see to what extent a similar relation between the  $k_l$  and  $v_{ll}$  exists.

A rigorous discussion of experimental data in the framework of the present formulation requires careful consideration of the contributions from orbital hyperfine interactions (that cause the chemical shift in molecules)  $K_{orb}$  and  $(T_1T)_{orb}$ , and of the choice of the zero of the shift scale. This will be left for later work, and here we will just give an illustration of the problems involved, using the parameters for Pt and Pd obtained by different authors [3, 13–17]. These are collected in table 1, where values marked with an asterisk are not from the original papers, but have been calculated for the present discussion. The experimental values of  $K$  and of  $(T_1T)^{-1}$  should be equal to the sums of the three contributions mentioned in the table; the experimental  $\chi$  has an additional diamagnetic contribution (estimated at roughly  $-20 \times 10^{-6}$  emu mol $^{-1}$ ). All authors use equations of the form (12), (13) and (16) for a two-band case, considering  $l = 0$  and  $l = 2$ , but they differ in the estimates of  $v_{00}$  and  $v_{22}$ . To obtain  $k_0$  and  $k_2$ , expressions analogous to (18) are used [12].

In the case of Pt (the first four columns of table 1), it is seen that setting the exchange integrals to zero can give either reasonably correct values for susceptibility and Knight shift (first column) or for relaxation rate and density of states (second column), but not for all quantities simultaneously. Introduction of a nonzero  $v_{22}$  improves the fit considerably

**Table 1.** Overview of NMR parameters used in the literature for Pt metal (columns 1–4) and Pd metal (columns 5 and 6). The reference numbers are given in the bottom row. The asterisked values are not from the original papers, but have been calculated for the discussion in the text.

$\nu_{00}$ (mRyd)	0	0	0	98	0	120
$\nu_{22}$ (mRyd)	0	0	29	37.7	0	29.4
$\chi_0$ ( $\mu\text{emu mol}^{-1}$ )	4.8	4.66*	10	14.8	6.2	13.5
$\chi_2$ ( $\mu\text{emu mol}^{-1}$ )	220	83.4*	215	206.5	710	746.5
$\chi_{orb}$ ( $\mu\text{emu mol}^{-1}$ )	13.2	—	18	9.9	30	20
$K_0$ (%)	1.02	0.99*	0.788	0.72	0.36	0.59
$K_2$ (%)	−4.65	−1.76*	−4.61	−4.38	−4.38	−4.55
$K_{orb}$ (%)	0.26	—	0.38	0.21	0.36	0.36
$(T_1 T)_0^{-1}$ ( $\text{s}^{-1} \text{K}^{-1}$ )	18.6*	17.5	11.1*	6.35	0.105*	0.19
$(T_1 T)_2^{-1}$ ( $\text{s}^{-1} \text{K}^{-1}$ )	77.4*	11.1	23.6*	19.7	3.11*	0.53
$(T_1 T)_{orb}^{-1}$ ( $\text{s}^{-1} \text{K}^{-1}$ )	134*	19.3	9.8*	7.25	1400*	0.41
$D_0$ ( $\text{Ryd}^{-1}$ )	2.02*	1.96	4.2	4.08	2.61*	3.34
$D_2$ ( $\text{Ryd}^{-1}$ )	92.6*	35.1	25.0*	20.4	299*	30.6
Reference	[14]	[3]	[13]	[15]	[16]	[17]

(column 3), and using both  $\nu_{22}$  and  $\nu_{00}$  an exact fit can be obtained (column 4). Pd NMR has been found in only one nonmetallic system [18]. The zero of the shift scale has been determined from measurements in the metal, assuming that the experimental susceptibility is essentially equal to  $\chi_2$ , the other contributions cancelling each other. The value of  $K$  reported in column 5 of table 1 is not corrected for the diamagnetic shift due to the core electrons, and corresponds to  $\gamma^{105} = 0.1942 \text{ kHz G}^{-1}$ . On this scale, the chemical shifts of the two samples of  $\text{PdCl}_6^{2-}$  in [18] are  $\delta = +5480 \text{ ppm}$  and  $\delta = +5398 \text{ ppm}$ . As in the case of Pt, the assumption of zero exchange integrals (column 5 of table 1) leads to unrealistic values for density of states and relaxation rate (the experimental value is  $T_1 T = 1.35 \text{ s}^{-1} \text{K}^{-1}$  [19]), but a good fit is obtained by allowing nonzero values (column 6).

The quality of the fits (that are close to experimental accuracy) in columns 4 and 6 of table 1 is not so much due to the use of better theoretical values for  $D_0$  and  $D_2$  as to the introduction of the factor  $k_2$ . Its justification has remained largely empirical however; no earlier theoretical treatment describing simultaneously the effect of core polarization (expressed by  $H_{hf,2}$  in (14)) and exchange enhancement (described by  $\nu_{22}$  and  $k_2$  in (11) and (17)) seems to be available.

## References

- [1] Winter J 1971 *Magnetic Resonance in Metals* (Oxford: Clarendon)
- [2] Narath A 1967 *Hyperfine Interactions* ed A J Freeman and R B Frankel (New York: Academic)
- [3] Yafet Y and Jaccarino V 1964 *Phys. Rev.* **133** A1630
- [4] Obata Y 1963 *J. Phys. Soc. Japan* **18** 1020
- [5] Vosko S H and Perdew J P 1975 *Can. J. Phys.* **53** 1385
- [6] Gunnarson O 1976 *J. Phys. F: Met. Phys.* **6** 587
- [7] Janak J F 1977 *Phys. Rev. B* **16** 255
- [8] Williams A R and von Barth U 1983 *Theory of the Inhomogeneous Electron Gas* ed S Lundquist and N H March (New York: Plenum)
- [9] Moriya T 1963 *J. Phys. Soc. Japan* **18** 516
- [10] Narath A and Weaver H T 1968 *Phys. Rev.* **175** 373
- [11] Bhattacharyya P, Pathak K N and Singwi K S 1971 *Phys. Rev. B* **3** 1568
- [12] Shaw R W and Warren W W 1971 *Phys. Rev. B* **3** 1562
- [13] Shaham M, El-Hanany U and Zamir D 1978 *Phys. Rev. B* **17** 3513

- [14] Clogston A M, Jaccarino V and Yafet Y 1964 *Phys. Rev.* **134** A650
- [15] Bucher J P and van der Klink J J 1988 *Phys. Rev. B* **38** 11 038
- [16] Seitchik J A, Gossard A C and Jaccarino V 1964 *Phys. Rev.* **136** A1119
- [17] Bucher J P 1988 *PhD Thesis* EPFL
- [18] Fedotov M A and Likholobov V A 1984 *Bull. Acad. Sci. USSR—Div. Chem. Sci.* **33** 1751
- [19] Takigawa M and Yasuoka H 1982 *J. Phys. Soc. Japan* **51** 787